Stringfellow, W.T. , R.D. Hines, D.K. Cockrum, and S.T. Kilkenny. 2000. "Factors Influencing Biological Treatment of MTBE in Fixed-Film Reactors." In: G.B. Wickramanayake, et al. (Eds.), Bioremediation and Phytoremediation of Chlorinated and Recalcitrant Compounds, pp. 175-181. Battelle Press, Columbus, OH.

FACTORS INFLUENCING BIOLOGICAL TREATMENT OF MTBE IN FIXED FILM REACTORS.

William T. Stringfellow (Lawrence Berkeley National Laboratory, Berkeley, CA)
Robert D. Hines (Envirex/U. S. Filter, Waukesha, WI)
Dirk K. Cockrum (Camp, Dresser & McKee Inc., Denver, CO)
Scott T. Kilkenny (Kinder Morgan Energy Partners, Orange CA)

ABSTRACT: Data from fluidized bed bioreactors treating contaminated ground water at two field sites have been collected and compared to laboratory studies with the objective of improving the reliability of methyl *tert*-butyl ether (MTBE) biotreatment in the field. Laboratory studies demonstrated that MTBE biodegradation was inhibited by a broad range of compounds, including o-xylene, methanol, toluene, and trichloroethylene (TCE). The general inhibition of MTBE degradation is similar to effects previously observed with nitrifying bacteria. Field data was examined to determine if two inhibitors, toluene and TCE, could be shown to effect MTBE treatment in fluidized bed reactors. It was found that there is a higher probability of poor MTBE removal efficiency during periods of higher toluene loading, but inhibition by TCE was not conclusively demonstrated. Results also show that periods of poor treatment also occur independently of effects attributable to toluene loading alone. These results illustrate the complexity of MTBE treatment and the limitations of using laboratory results to predict results in the field.

INTRODUCTION

MTBE has been used as a gasoline additive since 1979. As a consequence, MTBE is now a widespread environmental contaminant. Many gasoline and fuel transfer stations have MTBE contaminated ground water that must be recovered and treated before either re-injection or discharge. Activated carbon adsorption is currently the most widely used technology for the treatment of MTBE contaminated water.

Activated carbon is an effective treatment regime for MTBE, but has draw-backs. Activated carbon does not have a large sorption capacity for MTBE. It is also a phase transfer technology that does not result in the ultimate destruction of the MTBE. The spent carbon must be shipped off site for disposal or other treatment. Thus, there is a strong interest in developing alternative treatments for MTBE contaminated groundwater.

Our research has focused on the development of biological treatment as a viable, field-ready alternative for MTBE treatment at larger MTBE contaminated sites. We are developing biotreatment as both a stand alone technology and as a technology to be used in conjunction with carbon filters. Biological treatment

also has potential for the treatment of *tert*-butyl alcohol and other contaminants that are not efficiently treated by activated carbon filtration.

The focus of this work has been the evaluation and application of up-flow, fluidized-bed bioreactor technology for MTBE treatment under real world conditions. Fluidized-bed bioreactors have been widely applied for the treatment of ground water contaminated with gasoline hydrocarbons. The objective of our research is to understand the mechanism of MTBE degradation in these types of bioreactors and to delineate the parameters controlling MTBE treatment efficiency. In this paper we examine MTBE degradation efficiency in the presence of other groundwater contaminants, specifically toluene and TCE.

MATERIALS AND METHODS

Field sites. Data were collected from two field sites for this study. The Sparks Solvent Fuel Site (SSFS) is a fuel transfer terminal located in Sparks, NV. The Mission Valley Terminal (MV) is a smaller fuel transfer terminal located in San Diego, CA. Both sites have fluidized-bed bioreactors designed by Envirex/U. S. Filter that contain granular activated carbon (GAC) as a support media. Envirex/U. S. Filter bioreactors were installed at SSFS in 1995 for gasoline hydrocarbon treatment and began degrading MTBE in 1996. MTBE removal was demonstrated to be due to biological degradation (Stringfellow 1998). SSFS has a pair of 183 cm diameter reactors that are operated in parallel. MV has one 51 cm diameter reactor. The effective reactor volume at SSFS is approximately 17,600 liters and the MV reactor is approximately 680 liters. At SSFS, the reactors are an integral component of the MTBE control strategy. Fluidized bed bioreactors are being piloted at MV. Data from SSFS was collected as part of the requirements for regulatory compliance. Data from MV was collected as part of two separate pilot studies conducted at the site. For this paper, data from both MV studies have been pooled as one data set. All analyses were conducted using EPA approved methods at a contract analytical laboratory. Table 1 summarizes the operational conditions for the two sites.

TABLE 1: Summary of reactor flow and loading conditions for Envirex/U.S. Filter fluidized-bed bioreactors at Sparks Solvent Fuel Site, NV and Mission Valley, CA.

	SSFS Mean	MV Mean
Influent Flow Rate, liters per minute	700	16
Hydraulic Retention Time, hour	0.2	0.8
MTBE Concentration, µg/L	245	6,970
MTBE Load, mg/L-reactor volume/day	18	259

Laboratory studies. Samples of bed material from SSFS were collected and shipped on ice overnight to Lawrence Berkeley National Laboratory for testing. The bed material consisted of GAC coated with a microbial biofilm. Samples of GAC were placed in 40 mL glass vials, supplemented with a mineral salts buffer, and spiked with a solution of MTBE in water to give the appropriate final MTBE concentration required for each experiment. The vials contained 10 mL of liquid, approximately 30 mL of headspace, and were capped with Teflon vial caps. Compounds tested as inhibitors were added through the vial caps using a 10 μL syringe. MTBE was monitored by analysis of 100 μL head-space samples using a flame ionization detector after gas chromatographic separation. Samples were tested in triplicate for inhibition studies. Kinetic analysis was conducted using single vials for each concentration point. Initial degradation rates were measured after allowing for rapid equilibrium of the MTBE with the GAC sample.

RESULTS AND DISCUSSION

In order to examine the effects of other ground water constituents on MTBE degradation potential, batch experiments were conducted using GAC from SSFS. Initial MTBE degradation rates were reduced in vials receiving an additional compound in comparison to those vials receiving MTBE alone (Table 2). Most of the inhibitors tested (toluene, p-xylene, and methanol) were degraded over time, typically within three days, and MTBE degradation continued until all MTBE was degraded. Analysis of the headspace showed the vial still contained significant amounts of oxygen at the end of the experiment. Inhibition by TCE followed a different pattern in that the TCE was not degraded and MTBE degradation did not go to completion.

TABLE 2: Inhibition of initial MTBE biodegradation rates by bacteria grown as a biofilm on granular activated carbon. Data presented are means of three replicates.

Inhibitor	Initial MTBE Degradation Rate, % of Control	Final Inhibitor Concentration, % of Initial Concentration	Final MTBE Concentration, % of Initial Concentration
Toluene (430 mg/L)	25	0	0
TCE (1000 mg/L)	29	13	57
***p*-Xylene (170 mg/L)**	44	0	0
Methanol (500 mg/L)	33	0	0

These results suggest that MTBE degradation rate can be influenced by the presence of many other compounds. The broad sensitivity of MTBE

degradation activity is reminiscent of observations made with nitrifying bacteria. Nitrifying bacteria and ammonia removal in water treatment plants are well known to be sensitive to a broad range of inhibitors, including solvents and metals (Eckenfelder 1980). The exact reason for this sensitivity is not well understood.

The inhibitory effect of toluene and TCE on MTBE degradation was investigated further by conducting kinetic experiments using a constant toluene (520 mg/L) and TCE (400 mg/L) concentration and varying the initial MTBE concentration between 2 and 400 mg/L. Results from these experiments are presented as Lineweaver-Burk plots in Figure 1a and 1b. Lineweaver-Burke analysis allows the mechanism of inhibition to be investigated by comparing the slopes of linear fits of reaction rate data collected with MTBE plus an inhibitor and with MTBE only. In the case of both TCE and toluene, the lines intercept at the x-axis, suggesting the inhibition is due to a non-specific mechanism (non-competitive inhibition).

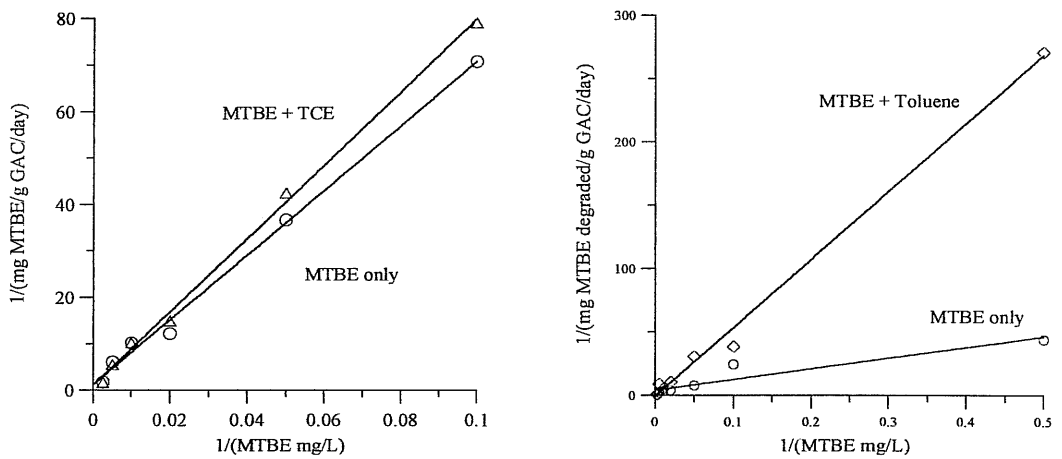


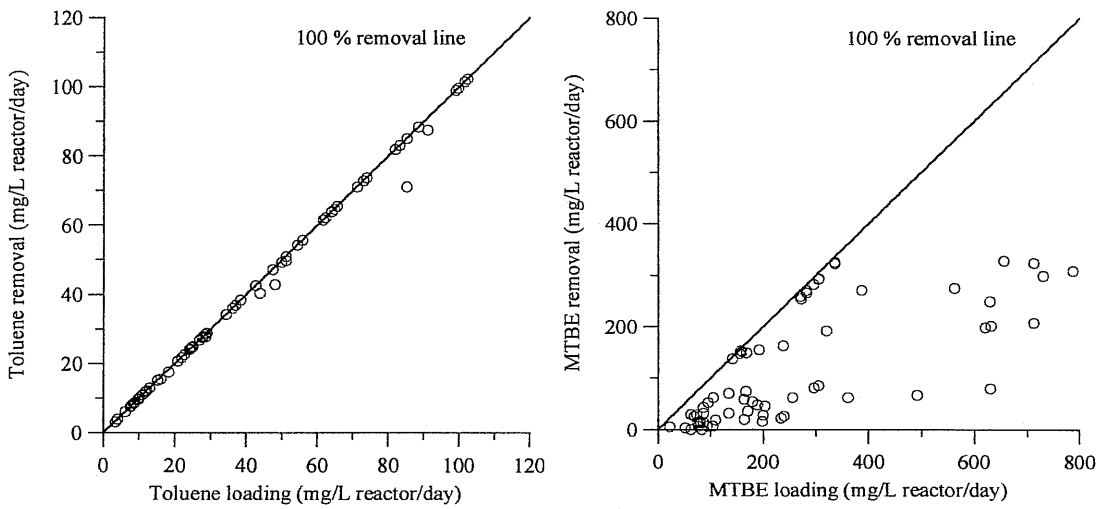
FIGURE 1. Lineweaver-Burke analysis of kinetic experiments examining the concentration dependent rates of MTBE degradation in the presence of toluene and trichloroethylene (TCE).

Given laboratory results, the question arises as to what relevance these results may have on understanding the operation of the field reactors. Both the full-scale reactors (at SSFS) and the pilot-scale reactor (at MV) have MTBE biodegrading populations present. In laboratory studies, GAC samples from both sites have consistently high MTBE degrading activity, even for samples collected during periods when the field systems have poor MTBE removal efficiency. Both sites have MTBE removal efficiencies that can fluctuate greatly, but also have demonstrated stable MTBE removal (greater than 90%) for extended periods. SSFS exhibited greater than 90% removal for periods longer than 100 days and 80% removal consistently for over 200 days. Both sites have maintained benzene removal efficiencies greater than 99% during their entire history of operation, even during periods when MTBE removal was completely lost. Based on these observations and our laboratory results, we postulated that toluene or TCE

inhibition could be a contributing factor in the loss of MTBE removal efficiency in field reactors.

One approach to answering this question is to plot removal efficiency data as a function of plant loading conditions. The SSFS treatment system receives very little toluene (mean < 2 μg/l), but some TCE (mean = 6 μg/L). In contrast the MV system receives significant amounts of toluene (mean = 1,150 μg/L) and does not receive TCE (non-detectable on all analysis). These differences can allow us to examine the influence of these parameters independently at the two sites.

Toluene and MTBE loading and removal rate data for MV are presented in Figure 2a and 2b. Toluene removal rates remained high during the complete course of this study. The maximum toluene loading capacity for this system has not been reached (Figure 2a). Unlike toluene, MTBE removal rate is not simply a direct function of MTBE loading at MV (Figure 2b). Figure 2b indicates that MTBE removal rate may reach a maximum of approximately 300 mg MTBE per liter reactor volume per day in this system.



a. **b.**

FIGURE 2. Loading and removal plots for the Mission Valley Fuel Transfer Station, CA.

MTBE removal efficiency as a function of toluene loading at MV was examined. Toluene loading and MTBE loading are not correlated in this system (r^2 = 0.075, n = 67), so the influence of toluene loading can be examined independently. Figure 3 is a plot of MTBE removal efficiency as a function of toluene loading. At toluene loading above 40 mg per liter reactor volume per day, MTBE removal efficiency was 60% or less (Figure 3). However, there were days where MTBE removal efficiency was low when toluene loading was low, indicating that toluene loading is only one of many factors that influence MTBE removal in this type of fluidized bed bioreactor.

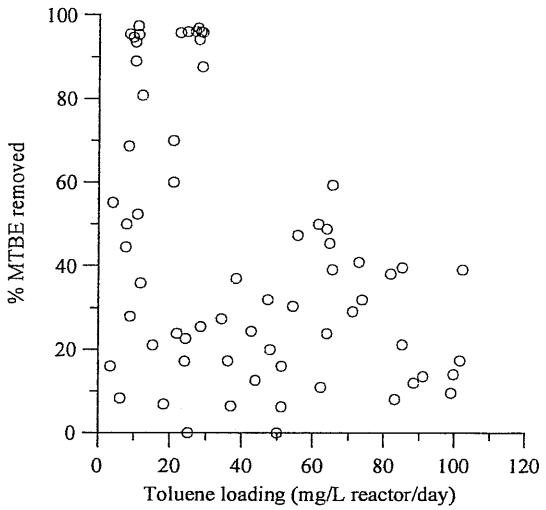
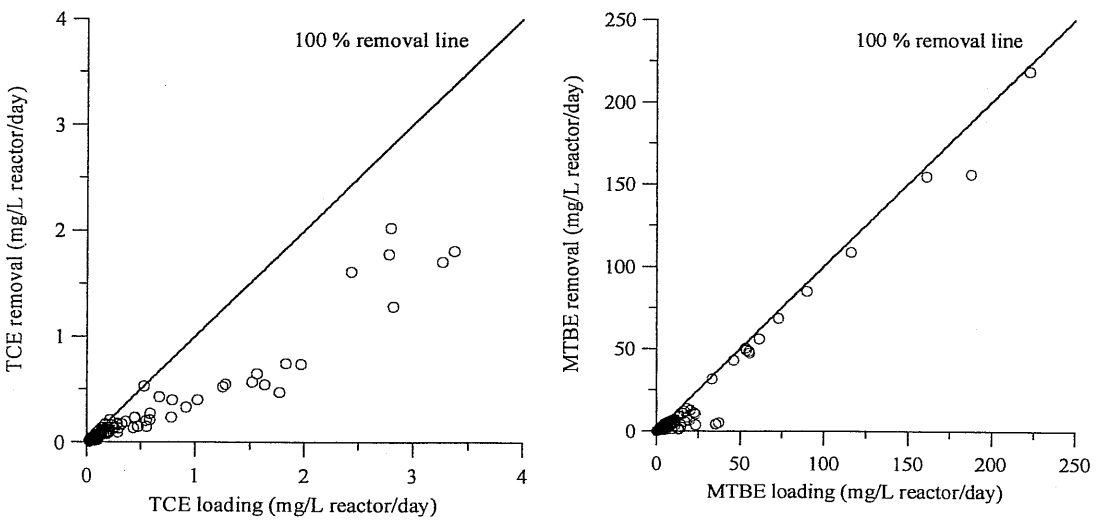


FIGURE 3. Methyl *tert*-butyl ether removal efficiency as a function of toluene loading at Mission Valley Terminal, CA.

A similar analysis has been conducted using data from SSFS. TCE and MTBE loading and removal efficiency data for MV are presented in Figure 4a and 4b. TCE removal averaged approximately 56% for the period included in this study. MTBE loading rates at SSFS are less than at MV (Table 1 and Figures 2b and 4b). The SSFS reactors exhibit a more consistent relationship between MTBE loading rates and MTBE removal rates. MTBE removal appears to be more stable at higher loading rates (Figure 4b).



a. **b.**

FIGURE 4. Loading and removal plots for the Sparks Solvent Fuel Site, NV. TCE removal rates are stable, but consistently less than 100%.

MTBE removal efficiency is plotted as a function of TCE loading in Figure 5. MTBE removal efficiency is consistently below 20% when TCE loading exceeds 2 mg per liter reactor volume per day, however there are very

few days when TCE loading is at this level. The data may indicate that TCE has a negative influence on MTBE removal efficiency, but the information is hardly conclusive. In any case, the analysis indicates that there are few days when TCE loading could be high enough to warrant concern as an operating variable for MTBE removal control.

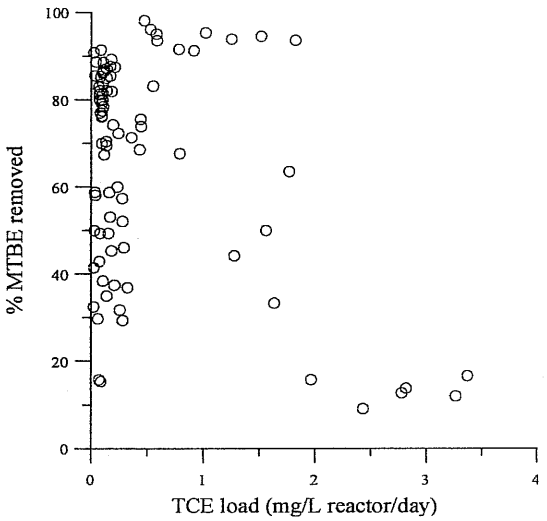


FIGURE 5. Methyl *tert*-butyl ether removal efficiency as a function of trichloroethylene (TCE) loading at Sparks Solvent Fuel Site, NV.

CONCLUSIONS

It can be concluded from this study that experiments examining factors influencing MTBE biodegradation conducted in the laboratory are useful for defining broad issues. However, laboratory studies have limitations in their ability to guide operation of field reactors. It appears that co-occurring compounds can influencing the treatment of MTBE in fluidized bed bioreactors, but the relationship is complicated by multi-variable interactions. Toluene and TCE removal rate varies as a direct function of loading in these reactors. In contrast, MTBE removal is not obviously a function of any one loading variable alone. This analysis indicates that MTBE removal in these systems is more difficult to predict and maintain than either toluene or TCE removal.

ACKNOWLEDGMENTS

This research was funded by a grant from Kinder Morgan Energy Partners to the Department of Energy, Lawrence Berkeley National Laboratory.

REFERENCES

Stringfellow, W. T. 1998. Biodegradation of methyl *tert*-butyl ether by microorganisms found in a groundwater treatment system. Abstracts of the 98th Annual Meeting of the American Society for Microbiology, Atlanta, GA, May 17 - 21.

Eckenfelder, W. W. 1980. Principals of Water Quality Management p. 315-325. CBI Publishing Company, Inc., Boston, MA.